Electrodeposition of thick palladium coatings from a palladium(II)-containing ionic liquid †

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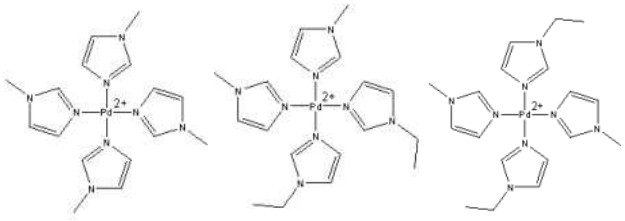
The first palladium-containing Liquid Metal Salts (LMS) are presented and shown to be suitable electrolytes for the electrodeposition of palladium. The homoleptic LMS of formula $[Pd(MeIm)_4][Tf_2N]_2$ or $[Pd(EtIm)_4][Tf_2N]_2$ (MeIm = *N*-methylimidazole, EtIm = *N*-ethylimidazole) have higher melting points than the heteroleptic $[Pd(MeIm)_2(EtIm)_2][Tf_2N]_2$, which proved to be the most promising electrolyte. The deposition reaction in these LMS was found to be irreversible but smooth and dense palladium layers can be deposited that are crack-free up to a thickness of 10 micron.

Palladium is a ductile, silvery-white platinum-group metal. Nowadays, its main uses are in the electronics industry and as catalyst in the automotive industry. The interest in palladium, as an alternative for gold in electrical contacts, is twofold: (1) due to its lower cost and (2) because its properties such as wear resistance and ductility are superior to those of gold. The electrodeposition of palladium from aqueous solutions is hampered by hydrogen embrittlement.[1] This is due to the very low overvoltage for hydrogen evolution on palladium and because palladium needs to be very strongly complexed in order to keep it in solution. Due to this strong coordination, the deposition potential becomes close or even lower than the potential where hydrogen is evolved. A third reason is that palladium has the highest hydrogen absorption capacity of all platinum-group metals, which leads to highly-stressed and largely cracked deposits when the thickness exceeds a few micron.[1] The electrodeposition of palladium from non-aqueous solvents such as ionic liquids is therefore an interesting alternative to aqueous electroplating. Sun and Hussey reported on the electrochemistry of palladium in chloroaluminate ionic liquids.[2] In these solutions, palladium is present as $[PdCl_4]^{2-}$ and the deposited palladium metal was a black, finely divided, poorly adherent powder. Chloroaluminates and chloride-based ionic liquids were used by other authors as well[3–9] but ionic liquids without halides are gaining interest. Examples are ionic liquids with dicyanamide and bis(trifluoromethylsulfonyl)imide ($[Tf_2N]^-$) anions.[10–13] Also deep-eutectic solvents have been studied as electrolytes for electrodeposition of palladium.[6] The deposition of alloys of palladium with other metals such as nickel, silver, indium, ruthenium, rhodium and gold have also reported too.[7–10,14] Palladium deposits from ionic liquids are often nodular,[9] dendritic,[5] show low adherence[8] or have a smooth morphology only at very low current densities ($0.001-0.01$ A dm^{-2}).[6] In this paper we report on the electrodeposition from palladium-containing Liquid Metal Salts (LMS). A LMS is an ionic liquid where a metal ion is incorporated in the structure of one of the ions.[15–26] Incorporation of a metal in the cation of the ionic liquid is an advantage for electrodeposition of metal layers at high current densities. This was shown for LMS containing copper and silver.[15–19] In this communication, we extend the LMS methodology to palladium. Compounds of formula $[Pd(AlkIm)_4][Tf_2N]_2$ (Fig. 1; AlkIm = *N*-alkylimidazole) were synthesized by reaction between palladium(II) acetate, *N*-alkylimidazoles and HTf_2N in acetonitrile. The compound $[Pd(MeIm)_4][Tf_2N]_2$ with *N*-methylimidazole ligands



(a) (b) (c)

Fig. 1 Structures of the cations of (a) $[Pd(MeIm)_4][Tf_2N]_2$, (b) *cis*-$[Pd(MeIm)_2(EtIm)_2][Tf_2N]_2$ (c) *trans*-$[Pd(MeIm)_2(EtIm)_2][Tf_2N]_2$.

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melted at 105 °C and the compound with *N*-ethylimidazole ligands, $[Pd(EtIm)_4][Tf_2N]_2$ melted at 76 °C. These melting points are quite high and previously we have found that heteroleptic compounds have lower melting points than their homoleptic equivalents.[18] Therefore, we also synthesized the heteroleptic compound $[Pd(MeIm)_2(EtIm)_2][Tf_2N]_2$, with a melting point of 45 °C. All three compounds were thoroughly characterised and their crystal structures determined (see ESI). The crystal structures determinations of all three compounds showed the expected square-planar coordination for the Pd(II) centre (Fig. 2). Bond distances and

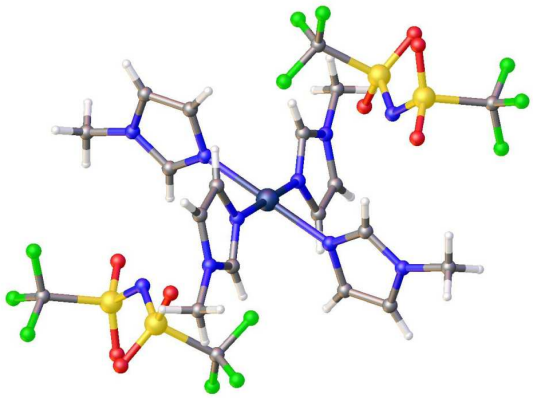

Fig. 2 View of the crystal structure of $[Pd(MeIm)_4][Tf_2N]_2$ showing the cation and two anions (disorder of the $[Tf_2N]^-$ anions omitted for clarity).

angles at the Pd(II) were in good agreement with other Pd(II) complexes with four imidazole ligands.[27] The crystal structure determination of $[Pd(MeIm)_2(EtIm)_2][Tf_2N]_2$ was complicated by the fact that the compound has two possible isomers: *cis*-$[Pd(MeIm)_2(EtIm)_2][Tf_2N]_2$ and *trans*-$[Pd(MeIm)_2(EtIm)_2][Tf_2N]_2$. In the crystal structure the ethyl group appears as a 50% disorder with the methyl group over all four AlkIm ligands indicating that there is no preference of *cis* over *trans* and the two configurations appear as a mixture. Thermogravimetric analysis (TGA) of $[Pd(MeIm)_2(EtIm)_2][Tf_2N]_2$ shows that the compound already loses a small amount of mass on heating at 5 °C min.$^{-1}$ between 25 and 100 °C (see ESI). Above 100 °C, the rate of loss increases and at 200 °C approximately the mass of one AlkIm ligand is lost. A second ligand lost at around 250 °C and starting from 330 °C, the remaining ligands are expelled together with the bistriflimide anions. Mass loss is complete at 450 °C with close to the theoretical value of 10.4% palladium remaining. Due to the mass loss between 25 and 100 °C, $[Pd(MeIm)_2(EtIm)_2][Tf_2N]_2$ is thus less thermally stable than LMS based on silver with imidazole ligands[17,18] so the electrodeposition experiments were carried out at the lower temperature of 70 °C, a compromise between thermal stability and a reasonably low viscosity (see ESI for viscosity data). A cyclic voltammogram of $[Pd(MeIm)_2(EtIm)_2][Tf_2N]_2$ on a gold working electrode (Fig. 3(a), solid line) shows a nu-

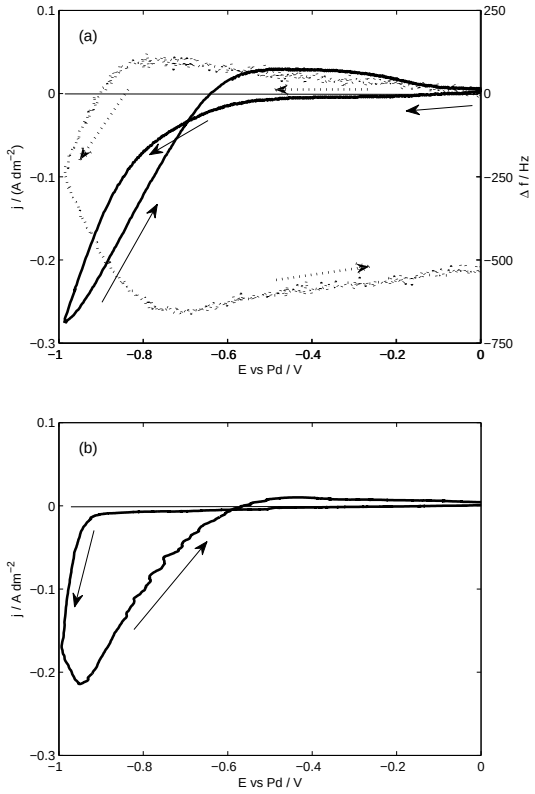

Fig. 3 (a) Cyclic voltammogram on Au (solid line) of $[Pd(MeIm)_2(EtIm)_2][Tf_2N]_2$ with QCM analysis (dotted line), (b) cyclic voltammogram on glassy carbon.

cleation loop (the backward scan crosses the forward scan) indicating that the deposition of palladium on gold from $[Pd(MeIm)_2(EtIm)_2][Tf_2N]_2$ requires a considerable overvoltage. On a glassy carbon electrode, the required overpotential is even larger than on gold (Fig. 3(b)). Furthermore, the current density during palladium reduction is low, especially when it is compared to the achievable current densities in LMS containing other metals.[15,17] The reaction

$$Pd^{2+} + 2e^- \rightarrow Pd \qquad (1)$$

is irreversible in $[Pd(MeIm)_2(EtIm)_2][Tf_2N]_2$. Not only is the cathodic charge much larger than the anodic charge, the irreversibility is also clear from a Quartz Crystal Microbalance analysis (QCM) (Fig. 3(a), dotted line): a negative shift in the Δf signal, indicating a mass deposited, starts when the potentials become more negative than -0.8 V together with an increase in the cathodic current. The Δf signal does not fall

back to zero which means that not all of the deposited mass can be redissolved. The positive shift in Δf during the cathodic scan is caused by a potential dependent adsorption or a change in damping of the QCM crystal.[28,29] A further analysis of the QCM data is given in ESI. The small anodic current in the backward scan is strongly dependent on the scan rate ν and reaches almost zero for low scan rates (see ESI). This proves the absence of an anodic Faradaic reaction and the irreversibility of reaction (1). The irreversibility might explain why the voltammogram is not centered at a potential of 0.0 V. vs the palladium quasi-reference electrode. It is expected that, if a wire of metal *M* is directly immersed into the solution, the reduction of metal ions M^{x+} should happen at negative potentials, and dissolution of metal *M* at positive potentials. If reaction (1) is irreversible however, the concentration of Pd(II) ions near the reference electrode is not in equilibrium with the palladium metal which gives a shift in the equilibrium potential. SEM micrographs of the morphologies of deposits are shown in Fig. 4(a) and 4(c). The thicknesses of

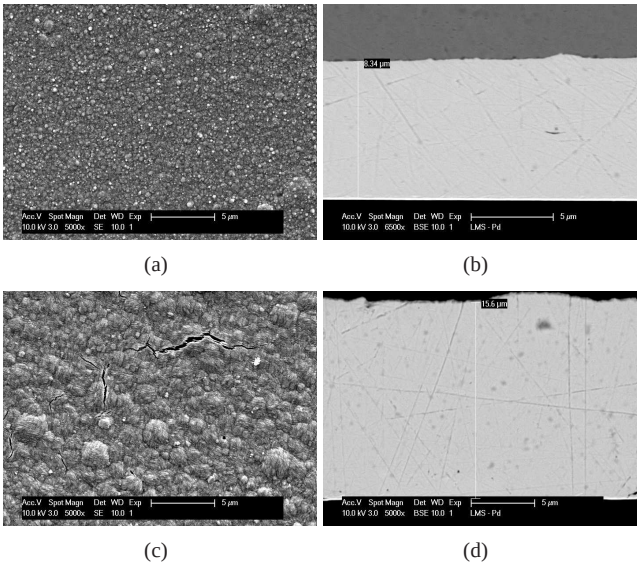

Fig. 4 Morphology (a,c) and cross-section (b,d) of deposits with different thicknesses from $[Pd(MeIm)_2(EtIm)_2][Tf_2N]_2$.

the deposits can be measured from the cross-sections shown in Figs. 4(b) and (d) and are 8.3 and 15.6 μm respectively. The deposits have an overall smooth morphology at reasonable current densities even in unstirred solutions, although the thicker deposit is slightly cracked. It is shown that thick, qualitative layers of palladium can be electroplated. Further studies are currently underway to deposit palladium-silver alloys, which are interesting for electrical contacts and catalysts.The authors acknowledge financial support by The Dow Chemical Company. The FWO-Flanders (Research Community "Ionic Liquids" and research project G0B9613N), the IWT-Flanders (SBO-project IWT 80031 "MAPIL"), the Hercules Foundation for supporting the purchase of the diffractometer (project AKUL/09/0035) and IoLiTec (Heilbronn, Germany) are also acknowledged. We thank Linda Stappers for her help with the QCM measurements.

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